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THE ANALYSIS OF N-NITROSODIMETHYLAMINE IN ENVIRONMENTAL SAMPLES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY.

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INTRODUCTION

N-nitrosodimethylamine (NDMA) is a potent carcinogen found in tobacco smoke, food and beverages, industrial processes, water treatment processes and in the biosphere. The identification of NDMA in drinking water samples resulted in the need for an accurate determination of NDMA in various aqueous samples at the low part per trillion (ppt) level. NDMA is very soluble in water and is therefore difficult to extract. Also, its polarity makes it difficult to chromatograph on standard non-polar phase columns. The presence of chemical interferences causes difficulties in the identification and quantitation of NDMA because of the common low mass ions that are monitored. These difficulties require that a method for NDMA be selective and sensitive. The advantages and disadvantages of the various GC/MS techniques are discussed.

EXPERIMENTAL SECTION

Extraction Procedure:

Particulates in the sample were removed by filtering the sample through pre-extracted glass wool. The internal standard, d_6-NDMA, was added to the sample and the sample mixed thoroughly. The pH of the sample was adjusted to 10-12 by addition of a sodium hydroxide solution. The sample was serially extracted three times with dichloromethane. The combined dichloromethane extract was washed with a dilute sulphuric acid (pH 2) solution and then filtered through anhydrous sodium sulphate. The extract was concentrated to 200 uL.

Low Resolution Mass Spectrometry (LRMS):

Full scan GC/MS work was done on a Finnigan 4500. The mass range scanned was m/z 35-510 in 0.80 seconds. GC analysis was performed on a DB-5 (60m x 0.32mm i.d.) column.

Selected ion monitoring (SIM) studies were performed on an HP-5970 MSD. The ions monitored for NDMA were m/z 74 and m/z 42 with dwell times of 150 ms and 50 ms, respectively. Ions monitored for d_6-NDMA were m/z 80 and m/z 46, with dwell times of 150 ms and 50 ms, respectively. A DB-1701 (30m x 0.25mm i.d.) column was used for the GC analysis. Additional SIM work was performed on the VG ZAB-2F at 1000 Resolving Power (RP).

High Resolution Mass Spectrometry (HRMS):

The VG ZAB-2F, a double focusing reverse geometry magnetic sector mass spectrometer, was tuned to 7000 RP for the high resolution work. A lockmass (m/z 68.9952, PFTBA) and the exact masses of NDMA (m/z 74.0480) and d_6-NDMA (m/z 80.0857) were monitored. Dwell times were 100 ms for m/z 74.0480 and 50 ms for m/z 68.9952 and m/z 80.0857.

Quantitation of NDMA was accomplished by standard isotope dilution.

RESULTS AND DISCUSSION

NDMA does not chromatograph well on a DB-5 column. Alternate phases that gave better chromatography and sensitivity were DB-17 and DB-1701. However, there were still problems with co-elution of interferences.

A single quadrupole mass spectrometer in the full scan mode does not have the sensitivity to detect low ppt levels of NDMA in drinking water. However, it offers a degree of selectivity because interferences can be monitored in the mass spectrum. The instrument detection limit was 10 ng injected on a DB-5 column routinely used for characterization of extractable organics. The method detection limit for full scan GC/MS was 2 ug/L.

The mass spectrum of NDMA consists of a molecular (quantitation) ion at m/z 74 (base peak) and an intense fragment (qualifying) ion at m/z 42 . In the SIM mode, using a single quadrupole mass spectrometer, sensitivity has been increased over full scan MS but some selectivity is lost due to the presence of co-eluting interferents with the same nominal masses, m/z 42, 74, 46 and 80. This limits the usefulness of a single quadrupole mass spectrometer for the determination of NDMA, as co-eluting interferences could give erroneous results. The instrument detection limit was 20 pg injected. The method detection limit was 25-50 ng/L. The linear dynamic range was from 20 pg to 15 ng.

The VG ZAB-2F at low resolution (1000 RP) in the SIM mode is more sensitive than a quadrupole mass spectrometer in SIM mode for the quantitation ion (m/z 74) (200 fg injected). However, due to the voltage switching technique m/z 42 is weak relative to m/z 74.

In order to detect low ppt levels of NDMA confidently, the effects of chemical interferences co-eluting with the NDMA must be eliminated. Methyl esters are a common compound class that give rise to ions at m/z 74. To differentiate them from the NDMA, the VG ZAB-2F was run > 7000 RP. NDMA samples run at > 7000 RP in the single ion monitoring mode had excellent sensitivity and selectivity. This permitted the low ppt detection of NDMA with an instrument detection limit of < 1 pg. Procedure blanks showed a 1-4 ng/L level of NDMA and therefore the method has a detection limit set at 5-10 ng/L. The linear dynamic range for these parameters was 2 pg to 40 ng.

CONCLUSION

Of the techniques evaluated, single ion monitoring at > 7000 resolution is the method of choice because of its superior sensitivity, selectivity and linear dynamic range. This allows the determination of NDMA in environmental samples to be at the low ppt level.

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